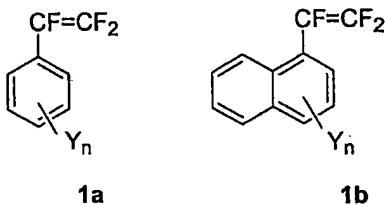


CLAIMS

What is claimed is:

1. A fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure **1a**, structure **1b** and mixtures thereof,

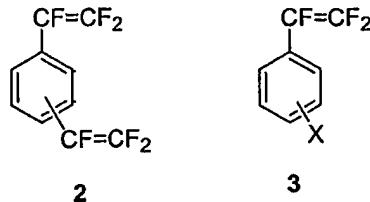


10

wherein  $\text{Y}$  is selected from the group consisting of  $-\text{R}_F\text{SO}_2\text{F}$  (sulfonyl fluoride),  $-\text{R}_F\text{SO}_3\text{M}$  (fluorosulfonic acid or salt),  $-\text{R}_F\text{SO}_2\text{NH}_2$  (fluorosulfonamide), and  $-\text{R}_F\text{SO}_2\text{N}(\text{M})\text{SO}_2\text{R}^2_F$  (imide); wherein  $\text{M}$  is H, an alkali cation, or ammonium; and  $\text{R}_F$  and  $\text{R}^2_F$  groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and  $n$  is between 1 and 2 for **1a**, or  $n$  is between 1 and 3 for **1b**.

2. The fluorinated ion exchange polymer of claim 1 wherein  $\text{Y}$  is  $-\text{R}_F\text{SO}_2\text{F}$ .
3. The fluorinated ion exchange polymer of claim 1 wherein  $\text{R}_F$  is selected from the group consisting of  $(\text{CF}_2)_q$  wherein  $q = 1$  to 20,  $(\text{CF}_2)_q\text{OCF}_2\text{CF}_2$  wherein  $q = 0$  to 12, and  $(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_q\text{CF}_2\text{CF}_2$  wherein  $q = 1$  to 8, and  $\text{R}^2_F$  is selected from the group consisting of methyl, ethyl, propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated.
- 25 4. The fluorinated ion exchange polymer of claim 3 wherein  $\text{R}_F$  is selected from the group consisting of  $(\text{CF}_2)_q$  wherein  $q = 1$  to 4,  $(\text{CF}_2)_q\text{OCF}_2\text{CF}_2$  wherein  $q = 0$  to 6, and  $(\text{CF}_2\text{CF}(\text{CF}_3)\text{O})_q\text{CF}_2\text{CF}_2$  wherein  $q = 1$  to 2, and  $\text{R}^2_F$  is selected from the group consisting of perfluoromethyl, perfluoroethyl, and perfluorophenyl.

5. The fluorinated ion exchange polymer of claim 1 wherein the grafting monomers further comprise co-monomers selected from the group consisting of compounds containing a single vinyl group, compounds containing multiple vinyl groups, monomers having the structure 2, monomers having structure 3 and mixtures thereof:



wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

10         6. The fluorinated ion exchange polymer of claim 5 wherein the compounds containing single or multiple vinyl groups are divinyl benzene or triallyl cyanurate.

15         7. The fluorinated ion exchange polymer of claim 5 wherein the substituents X on co-monomer of structure 3 are selected from the group consisting of hydrogen, halogen; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; and a perfluoroalkyl group containing oxygen, chlorine or bromine, wherein the perfluoroalkyl group comprises C1 to C10 carbon atoms.

20         8. The fluorinated ion exchange polymer of claim 7 wherein the substituents X on co-monomer of structure 3 are selected from the group consisting of hydrogen, chlorine, fluorine, methyl, ethyl, methoxy, perfluoromethyl, perfluoroethyl, perfluorobutyl, perfluoromethoxy, and  $-CF_2CF(CF_3)OCF_2CF_3$ .

25         9. The fluorinated ion exchange polymer of claim 1 wherein the base polymer is a homopolymer or copolymer of non-fluorinated, fluorinated, and perfluorinated monomers.

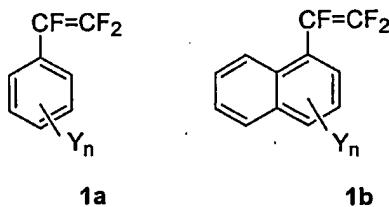
10. The fluorinated ion exchange polymer of claim 9 wherein the base polymer is selected from the group consisting of poly(ethylene-tetrafluoroethylene), poly(ethylene-chlorotrifluoroethylene),

poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoroalkyl vinyl ether), poly(tetrafluoroethylene-perfluoromethyl vinyl ether), poly(tetrafluoroethylene-perfluoropropyl vinyl ether),  
 5 polytetrafluoroethylene, modified polytetrafluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, poly(vinylidene fluoride-hexafluoropropylene), polyethylene, and polypropylene.

11. The fluorinated ion exchange polymer of claim 10 wherein the perfluoro(alkyl vinyl ether), is perfluoro(propyl vinyl ether) or perfluoro(ethyl vinyl ether).

10 12. The fluorinated ion exchange polymer of claim 2 wherein the base polymer comprises a terpolymer of ethylene, tetrafluoroethylene (TFE), and 1 to 10 mole% of a termonomer such as perfluorobutyl ethylene.

13. A fluorinated ion exchange polymer membrane comprising a  
 15 fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure 1a, structure 1b and mixtures thereof,



20 wherein Y is selected from the group consisting of -R<sub>F</sub>SO<sub>2</sub>F (sulfonyl fluoride), -R<sub>F</sub>SO<sub>3</sub>M (fluorosulfonic acid or salt), -R<sub>F</sub>SO<sub>2</sub>NH<sub>2</sub> (fluorosulfonamide), and -R<sub>F</sub>SO<sub>2</sub>N(M)SO<sub>2</sub>R<sup>2</sup><sub>F</sub> (imide); wherein M is H, an alkali cation, or ammonium; and R<sub>F</sub> and R<sup>2</sup><sub>F</sub> groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and  
 25 n is between 1 and 2 for 1a, or n is between 1 and 3 for 1b; and wherein the base polymer is a partially or completely fluorinated polymer in film form.

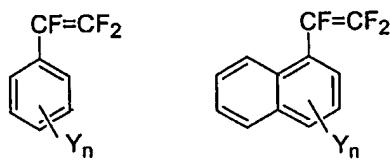
14. The fluorinated ion exchange membrane of claim 13 wherein the base polymer is a completely fluorinated polymer.

15. The fluorinated ion exchange membrane of claim 13 wherein the base polymer is selected from the group consisting of poly(ethylene-tetrafluoroethylene), poly(ethylene-tetrafluoroethylene-termonomer),  
 5 poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluorovinylether), polytetrafluoroethylene, poly(ethylene-chlorotrifluoroethylene); poly(vinylidene fluoride), and poly(vinylidene fluoride-hexafluoropropylene).

10 16. The fluorinated ion exchange membrane of claim 15 wherein the base polymer is selected from the group consisting of poly(ethylene-tetrafluoroethylene-termonomer), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoropropylvinylether), and poly(vinylidene fluoride).

15 17. The fluorinated ion exchange membrane of claim 15 wherein the base polymer comprises a terpolymer of ethylene, tetrafluoroethylene (TFE), and 1 to 10 mole% of a perfluorobutyl ethylene.

18. A grafting process for making the fluorinated ion exchange polymer membrane comprising:  
 20 forming an monomer composition comprising a grafting monomer, in neat form, emulsion form, or solution form, wherein the grafting monomer is selected from the group consisting of structure **1a**, structure **1b** and mixtures thereof,



25

**1a****1b**

wherein Y is selected from the group consisting of  $-R_FSO_2F$  (sulfonyl fluoride),  $-R_FSO_3M$  (fluorosulfonic acid or salt),  $-R_FSO_2NH_2$  (fluorosulfonamide), and  $-R_FSO_2N(M)SO_2R^2_F$  (imide); wherein M is H, an

alkali cation, or ammonium; and R<sub>F</sub> and R<sup>2</sup><sub>F</sub> groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and n is between 1 and 2 for 1a, or n is between 1 and 3 for 1b;

(b) irradiating a base polymer with ionizing radiation, and

5 (c) contacting the base polymer with the monomer composition from step (a), at a temperature of about 0 °C to about 120 °C for about 0.1 to about 500 hrs.

19. The process of claim 18 wherein the base polymer is in film form.

10 20. The process of claim 18 wherein steps (b) and (c) are performed simultaneously.

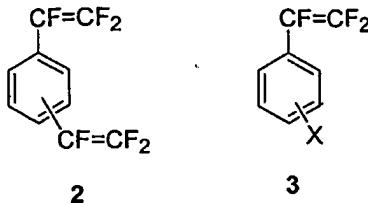
21. The process of claim 18 wherein steps (b) and (c) are performed sequentially.

22. The process of claim 18 wherein Y is -R<sub>F</sub>SO<sub>2</sub>F.

15 23. The process of claim 18 wherein R<sub>F</sub> is selected from the group consisting of (CF<sub>2</sub>)<sub>q</sub> wherein q = 1 to 20, (CF<sub>2</sub>)<sub>q</sub>OCF<sub>2</sub>CF<sub>2</sub> wherein q = 0 to 12, and (CF<sub>2</sub>CF(CF<sub>3</sub>)O)<sub>q</sub>CF<sub>2</sub>CF<sub>2</sub> wherein q = 1 to 8, and R<sup>2</sup><sub>F</sub> is selected from the group consisting of methyl, ethyl, propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated.

20 24. The process of claim 23 wherein R<sub>F</sub> is selected from the group consisting of (CF<sub>2</sub>)<sub>q</sub> wherein q = 1 to 4, (CF<sub>2</sub>)<sub>q</sub>OCF<sub>2</sub>CF<sub>2</sub> wherein q = 0 to 6, and (CF<sub>2</sub>CF(CF<sub>3</sub>)O)<sub>q</sub>CF<sub>2</sub>CF<sub>2</sub> wherein q = 1 to 2, and R<sup>2</sup><sub>F</sub> is selected from the group consisting of perfluoromethyl, perfluoroethyl, and perfluorophenyl.

25 25. The process of claim 18 wherein the grafting monomer further comprises co-monomers selected from the group consisting of compounds containing a single vinyl group, compounds containing multiple vinyl groups, monomers having the structure 2, monomers having structure 3 and mixtures thereof:



wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

26. The process of claim 25 wherein the compounds containing  
5 single or multiple vinyl groups are divinyl benzene or triallyl cyanurate.

27. The process of claim 25 wherein the substituents X on co-  
monomer of structure 3 are selected from the group consisting of  
hydrogen, halogen; linear or branched perfluoroalkyl groups, wherein the  
alkyl group comprises C1 to C10 carbon atoms; and a perfluoroalkyl group  
10 containing oxygen, chlorine or bromine, wherein the perfluoroalkyl group  
comprises C1 to C10 carbon atoms.

28. The process of claim 18 wherein the base polymer is a  
homopolymer or copolymer of non-fluorinated, fluorinated, and  
perfluorinated monomers.

15         29. The process of claim 28 wherein the base polymer is selected  
from the group consisting of poly(ethylene-tetrafluoroethylene),  
poly(ethylene-chlorotrifluoroethylene), poly(tetrafluoroethylene-  
hexafluoropropylene), poly(tetrafluoroethylene-perfluoroalkyl vinyl ether),  
poly(tetrafluoroethylene-perfluoromethyl vinyl ether),  
20         poly(tetrafluoroethylene-perfluoropropyl vinyl ether),  
polytetrafluoroethylene, modified polytetrafluoroethylene, polyvinyl fluoride,  
polyvinylidene fluoride, poly(vinylidene fluoride-hexafluoropropylene),  
polyethylene, and polypropylene.

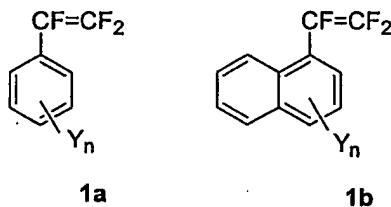
30. The process of claim 28 wherein the base polymer is a partially  
25         or completely fluorinated polymer.

31. The process of claim 30 wherein the base polymer is selected  
from the group consisting of poly(ethylene-tetrafluoroethylene),  
poly(ethylene-tetrafluoroethylene-termonomer), poly(tetrafluoroethylene-  
hexafluoropropylene), poly(tetrafluoroethylene-perfluorovinylether),

polytetrafluoroethylene, poly(ethylene-chlorotrifluoroethylene); poly(vinylidene fluoride), and poly(vinylidenefluoride-hexafluoropropylene).

32. A catalyst coated membrane comprising a polymer electrolyte  
 5 membrane having a first surface and a second surface, wherein the polymer electrolyte membrane comprises a fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure **1a**, structure **1b** and mixtures thereof,

10



wherein  $\text{Y}$  is  $-\text{R}_F\text{SO}_2\text{F}$  (sulfonyl fluoride),  $-\text{R}_F\text{SO}_3\text{M}$  (fluorosulfonic acid or salt),  $-\text{R}_F\text{SO}_2\text{NH}_2$  (fluorosulfonamide), or  $-\text{R}_F\text{SO}_2\text{N}(\text{M})\text{SO}_2\text{R}^2_F$  (imide);  
 15 wherein  $\text{M}$  is H, an alkali cation, or ammonium; and  $\text{R}_F$  and  $\text{R}^2_F$  groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and

$n$  is between 1 and 2 for **1a**, or  $n$  is between 1 and 3 for **1b**.

33. The catalyst coated membrane of claim 32 wherein the base  
 20 polymer is in film form.

34. The catalyst coated membrane of claim 32 further comprising at least one electrode prepared from an electrocatalyst coating composition present on the first and second surfaces of the polymer electrolyte membrane.

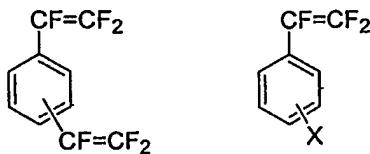
25 35. The catalyst coated membrane of claim 34 wherein the at least one electrode is an anode.

36. The catalyst coated membrane of claim 34 wherein the at least one electrode is a cathode.

37. The catalyst coated membrane of claim 34 wherein the electrocatalyst coating composition comprises a catalyst and a binder.

38. The catalyst coated membrane of claim 37 wherein the binder is a perfluorosulfonic acid polymer.

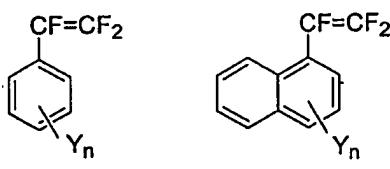
5       39. The catalyst coated membrane of claim 32 wherein the grafting monomer further comprises co-monomers selected from the group consisting of compounds containing a single vinyl group, compounds containing multiple vinyl groups, monomers having the structure 2, monomers having structure 3 and mixtures thereof:



10

wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

40. A membrane electrode assembly comprising a polymer electrolyte membrane, having a first surface and a second surface, 15 wherein the polymer electrolyte membrane comprises a fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure 1a, structure 1b and mixtures thereof,



20

1a

1b

wherein Y is -R<sub>F</sub>SO<sub>2</sub>F (sulfonyl fluoride), -R<sub>F</sub>SO<sub>3</sub>M (fluorosulfonic acid or salt), -R<sub>F</sub>SO<sub>2</sub>NH<sub>2</sub> (fluorosulfonamide), or -R<sub>F</sub>SO<sub>2</sub>N(M)SO<sub>2</sub>R<sup>2</sup><sub>F</sub> (imide); wherein M is H, an alkali cation, or ammonium; and R<sub>F</sub> and R<sup>2</sup><sub>F</sub> groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and

n is between 1 and 2 for 1a, or n is between 1 and 3 for 1b.

41. The membrane electrode assembly of claim 40 wherein the

base polymer is in film form.

42. The membrane electrode assembly of claim 40 further

5 comprising at least one electrode prepared from an electrocatalyst coating composition present on the first or second surfaces of the membrane.

43. The membrane electrode assembly of claim 42 wherein at least one electrode is an anode.

44. The membrane electrode assembly of claim 42 wherein at least 10 one electrode is a cathode.

45. The membrane electrode assembly of claim 42 wherein the electrocatalyst coating composition comprises a catalyst and a binder.

46. The membrane electrode assembly of claim 45 wherein the binder is a perfluorosulfonic acid polymer.

15 47. The membrane electrode assembly of claim 40 further comprising at least one gas diffusion backing adjacent at least one electrode present on the polymer electrolyte membrane.

48. The membrane electrode assembly of claim 40 further comprising at least one gas diffusion electrode present on the first or 20 second surfaces of the membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst coating composition.

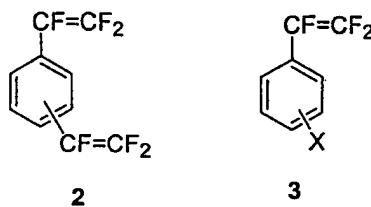
49. The membrane electrode assembly of claim 40 wherein Y is -R<sub>F</sub>SO<sub>2</sub>F.

25 50. The membrane electrode assembly of claim 40 wherein R<sub>F</sub> is selected from the group consisting of (CF<sub>2</sub>)<sub>q</sub> wherein q = 1 to 20, (CF<sub>2</sub>)<sub>q</sub>OCF<sub>2</sub>CF<sub>2</sub> wherein q = 0 to 12, and (CF<sub>2</sub>CF(CF<sub>3</sub>)O)<sub>q</sub>CF<sub>2</sub>CF<sub>2</sub> wherein q = 1 to 8, and R<sup>2</sup><sub>F</sub> is selected from the group consisting of methyl, ethyl,

propyl, butyl, and phenyl, each of which may be partially fluorinated or perfluorinated.

51. The membrane electrode assembly of claim 40 wherein the grafting monomers further comprise co-monomers selected from the group

5 consisting of compounds containing a single vinyl group, compounds containing multiple vinyl groups, monomers having the structure 2, monomers having structure 3 and mixtures thereof:



10 wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

52. The membrane electrode assembly of claim 51 wherein the compounds containing single or multiple vinyl groups are divinyl benzene or triallyl cyanurate.

15 53. The membrane electrode assembly of claim 51 wherein the substituents X on co-monomer of structure 3 are selected from the group consisting of hydrogen, halogen; linear or branched perfluoroalkyl groups, wherein the alkyl group comprises C1 to C10 carbon atoms; and a perfluoroalkyl group containing oxygen, chlorine or bromine, wherein the

20 perfluoroalkyl group comprises C1 to C10 carbon atoms.

54. The membrane electrode assembly of claim 41 wherein the base polymer is a homopolymer or copolymer of non-fluorinated, fluorinated, and perfluorinated monomers.

55. The membrane electrode assembly of claim 54 wherein the base polymer is selected from the group consisting of poly(ethylene-tetrafluoroethylene), poly(ethylene-chlorotrifluoroethylene), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluoroalkyl vinyl ether), poly(tetrafluoroethylene-perfluoromethyl vinyl ether), poly(tetrafluoroethylene-perfluoropropyl vinyl ether),

polytetrafluoroethylene, modified polytetrafluoroethylene, polyvinyl fluoride, polyvinylidene fluoride, poly(vinylidene fluoride-hexafluoropropylene), polyethylene, and polypropylene.

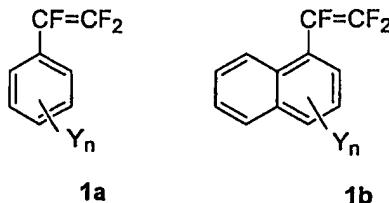
56. The membrane electrode assembly of claim 54 wherein the  
 5 base polymer is selected from the group consisting of poly(ethylene-tetrafluoroethylene), poly(ethylene-tetrafluoroethylene-termonomer), poly(tetrafluoroethylene-hexafluoropropylene), poly(tetrafluoroethylene-perfluorovinylether), polytetrafluoroethylene, poly(ethylene-chlorotrifluoroethylene); poly(vinylidene fluoride), and  
 10 poly(vinylidenefluoride-hexafluoropropylene).

57. The membrane electrode assembly of claim 56 wherein the base polymer comprises a terpolymer of ethylene, tetrafluoroethylene (TFE), and 1 to 10 mole% of a perfluorobutyl ethylene.

58. The fluorinated ion exchange polymer of claim 55 wherein the  
 15 perfluoro(alkyl vinyl ether), is perfluoro(propyl vinyl ether) or perfluoro(ethyl vinyl ether).

59. The membrane electrode assembly of claim 54 wherein the base polymer comprises a terpolymer of ethylene, tetrafluoroethylene (TFE), and 1 to 10 mole% of a termonomer such as perfluorobutyl  
 20 ethylene.

60. An electrochemical cell comprising a membrane electrode assembly, wherein the membrane electrode assembly comprises a polymer electrolyte membrane, having a first surface and a second surface, wherein the polymer electrolyte membrane comprises a  
 25 fluorinated ion exchange polymer prepared by grafting a monomer on to a base polymer, wherein the grafting monomer is selected from the group consisting of structure **1a**, structure **1b** and mixtures thereof,



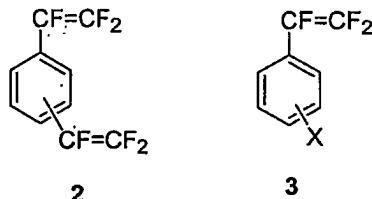
wherein Y is -R<sub>F</sub>SO<sub>2</sub>F (sulfonyl fluoride), -R<sub>F</sub>SO<sub>3</sub>M (fluorosulfonic acid or salt), -R<sub>F</sub>SO<sub>2</sub>NH<sub>2</sub> (fluorosulfonamide), or -R<sub>F</sub>SO<sub>2</sub>N(M)SO<sub>2</sub>R<sup>2</sup><sub>F</sub> (imide); wherein M is H, an alkali cation, or ammonium; and R<sub>F</sub> and R<sup>2</sup><sub>F</sub> groups are perfluorinated or partially fluorinated, and may optionally include ether oxygens; and

n is between 1 and 2 for 1a, or n is between 1 and 3 for 1b.

61. The electrochemical cell of claim 56 wherein the electrochemical cell is a fuel cell.

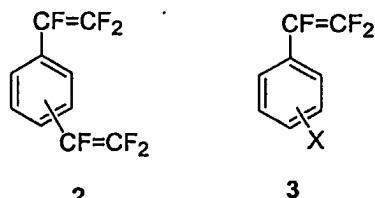
10 62. The electrochemical cell of claim 61 wherein the base polymer is in film form.

63. The electrochemical cell of claim 60 wherein the grafting monomers further comprise co-monomers selected from compounds containing single or multiple vinyl groups, such as divinyl benzene, triallyl cyanurate, or monomers having the structure 2 or 3



wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

20 64. The electrochemical cell of claim 61 wherein the grafting monomers further comprise co-monomers selected from compounds containing single or multiple vinyl groups, such as divinyl benzene, triallyl cyanurate, or monomers having the structure 2 or 3



25 wherein X is hydrogen, halogen, alkyl, or perfluoroalkyl that may include oxygen.

65. The fuel cell of claim 61 further comprising at least one electrode prepared from an electrocatalyst containing composition present on the first and second surfaces of the polymer electrolyte membrane.
66. The fuel cell of claim 60 further comprising at least one gas diffusion backing.
  - 5 67. The fuel cell of claim 61 further comprising a gas diffusion electrode present on the first and second surfaces of the membrane, wherein the gas diffusion electrode comprises a gas diffusion backing and an electrode prepared from an electrocatalyst containing composition.
- 10 68. The fuel cell of claim 61 further comprising a means for delivering a fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, hydrogen or methanol in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode.
- 15 69. The fuel cell of claim 64 further comprising a means for delivering a fuel to the anode, a means for delivering oxygen to the cathode, a means for connecting the anode and cathode to an external electrical load, hydrogen or methanol in the liquid or gaseous state in contact with the anode, and oxygen in contact with the cathode.
- 20 70. The fuel cell of claim 68 wherein the fuel is an alcohol or ether.
71. The fuel cell of claim 70 wherein the fuel is methanol.
72. The fuel cell of claim 68 wherein the fuel is hydrogen.